

PATENT SPECIFICATION

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1082,575



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COMPLETE SPECIFICATION

Improvements in Gaseous Fuel Cells

- We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 5, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to gaseous fuel cells, and is concerned with an improvement in or modification of the gaseous fuel cells described and claimed in the Specification of our co-pending Patent Application No. 40301 of 1963 (Serial No. 1,038,884) — hereinafter referred to as the "parent Application".
- The Specification of the parent Application describes and claims a gaseous fuel cell especially for use with carbonaceous gases which comprises an electrolyte comprising an aqueous solution of caesium and/or rubidium hydroxide, carbonate and/or bicarbonate positioned between and in direct electrical contact with a pair of gas permeable, electronically conductive electrode elements, means for supplying a fuel gas to one of said electrode elements and means for supplying an oxidant gas to the other of said electrode elements.
- As indicated, the Specification of the parent Application is directed to the use of carbonaceous fuels in the fuel cell. We have now discovered that the fuel cell is also suitable for use with a fuel comprising a compound of hydrogen and nitrogen, such as ammonia or hydrazine.
- According to the present invention there is provided a method of operating a gaseous fuel cell having an electrolyte comprising an aqueous solution of caesium and/or rubidium hydroxide, carbonate and/or bicarbonate positioned between and in direct electrical contact with a pair of gas permeable, electronically conductive electrode elements, which method comprises supplying one of said electrode elements with a fuel comprising a compound of hydrogen and nitrogen, and supplying the other of said electrode elements with an oxidant gas.
- The composition of the electrolyte of the present fuel cell, as well as the construction and composition of the electrode elements may be any of those described in the Specification of the parent Application, to which reference may be made for more details of such compositions and construction. However, since the fuels of the present invention are water-soluble, the concentration of the aqueous electrolyte comprising either the hydroxide, carbonate or bicarbonate of caesium or rubidium or a mixture of any or all of such compounds, should preferably be chosen so as to limit the solubility of the fuel so that it does not migrate unreacted to the cathode.
- With the cell of the present invention, when air or oxygen is used as the oxidant, the overall reaction is the oxidation of the fuel to nitrogen and water, the electrode reactions being as follows for ammonia:—
- Anode: $2\text{NH}_3 + 6\text{OH}^- = \text{N}_2 + 6\text{H}_2\text{O} + 6\text{e}^-$
- Cathode: $1\frac{1}{2}\text{O}_2 + 3\text{H}_2\text{O} + 6\text{e}^- = 6\text{OH}^-$
- Overall: $2\text{NH}_3 + 1\frac{1}{2}\text{O}_2 = \text{N}_2 + 3\text{H}_2\text{O}$
- Both nitrogen and water are produced at the anode and are withdrawn from the cell.
- Ammonia is a particularly desirable fuel because it is a gas at room temperature but may be stored as a liquid under pressure at room temperature, and produces a very high maximum power output, although not so high as hydrazine.
- The invention will now be illustrated by the following Examples.

[Price 4s. 6d.]

EXAMPLES 1 to 4

Two fuel cells were constructed as described in Example 4 of the Specification of the parent Application. In one cell oxygen was used as the oxidant and in the other cell air was used as the oxidant. Using ammonia as fuel and

aqueous caesium hydroxide solutions having boiling points 10°C. above the operating temperature of the cells, the performance of these cells was determined at 140° and 160°C. The results are given in the following Table.

	Current Density. ma/cm.	Example 1. O ₂ —140°C.	Example 2. Air—140°C.	Example 3. O ₂ —160°C.	Example 4. Air—160°C.
15	0	0.75	0.75	0.79	0.80
	100	0.64	0.60	0.66	0.68
	200	0.61	0.55	0.63	0.64
	400	0.56	0.45	0.62	0.62
	600	0.51	0.33	0.60	0.57
20	800	0.40	0.07	0.57	0.51
	1000	—	—	0.54	0.41
	1600	—	—	0.37	—

These fuel cells were operated for over 160 hours.

In the foregoing example, it is to be noted that the current is expressed in terms of current per unit area of electrode, i.e., milliamperes per square centimeter of electrode area and not in terms of the total current for the full area of the experimental cell.

WHAT WE CLAIM IS:—

1. A method of operating a gaseous fuel cell having an electrolyte comprising an aqueous solution of caesium and/or rubidium hydroxide, carbonate and/or bicarbonate positioned between and in direct electrical contact with a pair of gas permeable, electronically conductive electrode elements, which method comprises supplying one of said electrode elements with a fuel comprising a compound of hydrogen and nitrogen, and supplying the other of said electrode elements with an oxidant gas.

2. A method as claimed in Claim 1, where-

in the concentration of the aqueous electrolyte is chosen so as to limit the solubility of the fuel so that it will not migrate unreacted to the cathode.

3. A method as claimed in Claim 1 or 2, wherein the fuel is ammonia.

4. A method as claimed in Claim 1 or 2, wherein the fuel is hydrazine.

5. A method as claimed in any one of Claims 1 to 4, wherein the oxidant is air.

6. A method as claimed in any one of Claims 1 to 4, wherein the oxidant is oxygen.

7. A method of operating a gaseous fuel cell substantially as hereinbefore described in any one of the foregoing Examples.

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Int. Cl.:—C 08 g 53/08

COMPLETE SPECIFICATION

Improvements in or relating to Fluorocarbon Polymeric Matrices

5 We LEESONA CORPORATION, a corporation organized and existing under the laws of the Commonwealth of Massachusetts, United States of America of 333, Strawberry Field Road, Warwick, State of Rhode Island, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to the production of a porous hydrophobic matrix, having pre-determined wetting characteristics, useful as filters, separators, diaphragms and the like. More particularly, the invention relates to porous membranes or shaped articles of sinterable, corrosion and heat resistant fluoro-polymers. The invention will be described hereinafter with particular reference being made to elements such as porous barriers, supports in electrode construction, or matrices for retaining an electrolyte, for use in an electrochemical cell, and more particularly in a fuel cell. It is to be understood, however, that the materials of the invention have other utility where the peculiar characteristics of the composition are important as will be apparent to one skilled in the art. Reference to a fuel cell is by way of convenience and sets forth a preferred utility for the materials.

15 The principal requisites of a matrix or separator of the class useful in electrochemical cells are maximum chemical stability, low electrical resistance, and maximum diffusion of electrolyte in order to minimize the internal resistance of the over-all assembly. Other necessary properties include sufficient mechanical strength to withstand handling during assembly of the cell, shape and dimensional stability when wet with electrolyte, controlled porosity and sufficient density to act

as a physical barrier to resist penetration of the matrix by the gaseous reactants piercing the separator and possible short circuiting of the cell by metallic growths. 45

For optimum performance in a fuel cell employing a trapped aqueous electrolyte, the matrix should be wettable by the electrolyte to the extent that the electrolyte forms a continuous phase which is in intimate contact with one surface of each electrode. Moreover, the combination of matrix and electrolyte must act as an effective bubble barrier to avoid the mixing of reactant gases at one electrode surface and thus to prevent reactions of an explosive nature. The electrolyte matrix must also have a porosity sufficient to permit the necessary ionic mobility requisite to the ionic conductance internal to the cell structure at minimum resistivity and be inert to the electrolyte impregnated therein. To avoid a current flow within the electrolyte systems per se, with consequent wastage of utilizable power, the matrix must be an excellent electrical insulator. The matrix must also have a sufficient degree of pliability to conform to the surfaces of the electrodes of the cell so as to maintain the highest degree of area of contact therebetween and avoid areas of separation therefrom. Since the matrix must also function as a physical barrier to the mixing of the gaseous reactants, the matrix for a trapped electrolyte is ordinarily employed in fuel cell constructions wherein the matrix is compressed about the peripheral edges in sealing engagement with a suitable apertured framing members and/or cooperable sealing means or gasket. Therefore, the matrix preferably will have properties commendable to gasketing or sealing means. To minimize the cost the matrix should be constructed of materials which are 75 80

readily available and manufactured by a quick, easy, efficient process, and the matrix preferably should be re-utilizable by replenishing with fresh aqueous electrolyte.

5 Materials currently employed as matrices for trapped electrolyte systems include various materials such as modified cellulose and pressed mineral fibers such as asbestos, alumina, and magnesia. Such materials currently in use as matrix-forming materials suffer from a number of serious drawbacks, the principal among them being lack of chemical and/or thermal stability and poor mechanical strength. By way of example, asbestos impregnated with an aqueous alkali such as potassium hydroxide is readily attacked to produce gelatinous residues which interfere with the ionic conductance, increase internal cell resistance and are incapable of being reimpregnated with fresh electrolyte. Modified cellulose, on the other hand, is easily hydrolyzed by the electrolyte.

The use of microporous polymeric films as elements in electrochemical cells, such as battery separators, is not new. For example, United States Patents Nos. 2,542,527 and 2,676,929 disclose processes wherein polymeric materials such as polyvinyl chloride or polyethylene are admixed with finely-ground starch particles and the mixture cast into sheets. The starch particles are hydrolyzed and rendered soluble by successive treatments and washing in both acid and alkaline media, leaving in their place voids of the approximate size of the original particles. While this type of microporous material has found some commercial application in the battery art, its principal disadvantages are the relatively high cost of manufacture, the difficulty experienced during manufacture in maintaining control of the pore size in the finished product, mechanical weakness of the resultant matrix, and the inability of the process to achieve pores with surfaces of controlled wetting characteristics, which are desirable in many fuel cell applications.

Accordingly it is one object of the present invention to provide a method for fabricating a matrix free, or substantially free, of the defects associated with the aforementioned matrices of the prior art.

According to the invention there is provided a method for preparing porous shaped bodies comprising a hydrophobic polymeric matrix having preselected wettable characteristics, which method comprises the steps of precipitating a fluorocarbon polymer onto loose fibers having a charge opposite to that of said polymer to form a polymer-fiber aggregate, forming said aggregate into a desired shape, elevating said formed aggregate to a temperature at which said precipitated polymer will sinter, maintaining said aggregate at said temperature for a time sufficient to

cause said polymer to sinter and form a pliable and coherent mass and consume said fibres, thus exposing the volume previously occupied by said consumable fibers to ambient atmosphere.

The invention also provides a hydrophobic polymeric matrix having preselected wettable characteristics comprising a continuous phase of sintered fluorocarbon polymeric material having a series of integral interconnecting pores and a discontinuous colloidal mineral phase deposited in said pores, said mineral phase being uniformly arranged from major surface to major surface of said matrix.

The porous fluoropolymer matrix may be made by precipitating the polymer from a colloidal state onto a loose slurry of selected and oppositely charged fibers, such as cellulose fibers. The charge on the fibers is induced by the adsorption of cationic agents on their surface. The fiber/polymer ratio and the diameter of the fiber determine porosity and pore size, respectively. The plastic coated coagulum is extracted from the slurry and dried. The fibers may be either re-slurried in water and re-deposited upon a paper mat by processes known to the art or compressed into a sheet in a suitable mold. The dried sheet or mat is placed in a furnace adjusted to the sintering temperature of the hydrophobic polymer, causing the fibers to burn out, leaving a porous plastic structure behind.

Varying wetting characteristics and pore surface texture can be produced by adsorbing a colloidal mineral of desired dimensions onto the surface of the fiber in an aqueous medium and precipitating the finely divided particulate fluoro-polymer from an aqueous dispersion onto the mineral modified surface of the fiber, and collecting the resulting coagulum. The coagulum can be formed into any desired shape, which is then subjected to elevated temperatures sufficient to cause the particulate hydrophobic polymer to sinter to a pliable coherent mass and to cause the fibrous substrate to undergo combustion thus exposing the volume previously occupied by the fibrous substrate to the ambient atmosphere, and leaving the colloidal mineral distributed uniformly throughout the pore structure and firmly held therein. In an electrolyte matrix the mineral additives, or fillers, act as "stepping stones", allowing the "electrolyte" to achieve ionic conductive continuity between the electrodes as a result of their particular wetting characteristics. Any carbonaceous residue in the structure can be removed by treating the sintered material with a strong oxidizing acid, such as nitric acid, prior to the final drying. The resulting composition has a pore surface texture and chemical composition which is readily wettable by an aqueous electrolyte. The electrical resistivity of the porous material when

used as a matrix for a trapped electrolyte, or as a support for an electrode, is materially reduced and the ionic conductivity enhanced to a high degree.

5 In practicing the present invention, a staple
cellulosic or similar fiber of the desired di-
mensions can be suspended in an aqueous
medium by such conventional methods as the
action caused by a plurality of blades rotat-
10 ing at high speeds to produce a severing
action upon the fibrous material, and there-
by causing the formation of a pulp or sus-
pension of fibers corresponding to the de-
sired dimensions of the ultimate pore struc-
15 ture of the matrix. A colloidal mineral can
be added to the resulting suspension and
caused to sorb upon the surface thereof by
the addition of cationic agents or like means.

20 The particulate hydrophobic polymer is pre-
cipitated from a colloidal state into a loose
slurry of the fibers, or the polymer is added
to the aqueous dispersion of fibers, and a
coagulating or flocculating agent added to
25 cause coagulation or precipitation to form
a polymer/fiber coagulum, or a polymer/
colloidal mineral/fiber coagulum or aggregate.

30 The coagulum is capable of separation and
extrusion by conventional processes to form
articles of any desired shape suitable for
the ultimate purposes intended. The shaped
article is subjected to temperatures sufficient
to cause sintering of the particulate polymer,
causing formation of a coherent pliable mass
having a porosity controlled by the amount
35 of cellulosic fibers therein, through combus-
tion of the fibers forming a carbonaceous com-
bustion product and thereby exposing the
volume previously occupied by the cellulosic
fiber.

40 The preliminary coalescence of the poly-
mer/fiber, or polymer/colloidal mineral/
fiber aggregate to form the sinterable stock
of the present invention is accomplished by
an organic coalescing or flocculating agent
45 which is mixable with water and in which
the polymeric material is substantially in-
soluble. Exemplary flocculating or coalescing
agents include acetone, methyl ethyl ketone,
methanol and ethanol. The sinterable stock
50 from the initial coalescing can be formed into
membranes or other desired shapes through
conventional extrusion or orifices, extrusion
slots or by resuspension in an aqueous medium
and collection by mechanical means, such as
55 forced filtration of the aqueous phase.

60 Complete coalescence of the polymer par-
ticles to form a continuous polymeric phase
in the formation of the porous article is
achieved by sintering. Development of opti-
mum mechanical properties is dependent in
part upon the ratios of polymer:mineral:
fibrous substrate as well as in part upon the
sintering conditions, since incomplete sin-
65 tering results in weak spots and correspond-
ing poor mechanical properties. The optimum

sintering temperature appears to be approxi-
mately 350—400°C. although temperatures
as high as 430°C. can be successfully em-
ployed with some fluoro-polymers such as
polytetrafluoroethylene. In general, sintering
is effected at a temperature between the crys-
talline melt point, e.g., in the case of poly-
tetrafluoroethylene, 327°C., and the decom-
position temperature of the hydrophobic poly-
mer. While higher temperatures in general
require shorter sintering times, temperatures
70 in excess of 400°C., e.g. in the case of poly-
tetrafluoroethylene, tend to promote appre-
ciable degradation. Any suitable heating
media such as the hot air of a muffled
furnace, radiant heat, and heated rollers or
75 platens may be employed in the sintering
operation.

Although particular reference has been
made hereinbefore to polytetrafluoroethylene,
which is the preferred polymer in the practice
of the present invention, other polyhalogena-
ted polymers can be used. By way of example
copolymers of tetrafluoroethylene with other
unsaturated organic compounds such as per-
80 fluoropropylene and chlorotrifluoroethylene
may be employed provided such copolymers
maintain the essential properties of the tetra-
fluoroethylene homopolymer. In general, co-
polymerizable modifiers may be present in
an amount up to about 15% by weight of
the copolymer without destroying or deviating
from the advantageous properties of the tetra-
fluoroethylene. Other polymeric materials
usable herein are polymers of fluorinated pro-
85 pylene, vinylfluoride, vinylidene fluoride, and
copolymers thereof.

The production of the fluoro-polymer dis-
persion is not a part of the present inven-
tion. The dispersion may be prepared by any
suitable process described in the existing art
including, by way of example, procedures
disclosed in U.S. Patent No. 2,478,229; U.S.
Patent No. 2,534,058; U.S. Patent No.
2,559,750; and U.S. Patent No. 2,685,707.
100 The particle size of the polymer in the dis-
persions employable in the practice of the
present invention may vary over a wide range.
Preferably, the particles of the polymer should
be of a colloidal state, e.g., a practical size
range being from 0.05 to 5 microns and,
more preferably, from 0.1 to 3 microns in
size. The smaller the particles the more easily
is the formation of the sinterable stock and
the workup of the sinterable stock to the
ultimate, porous shaped structure. The fluoro-
polymer can vary widely as to molecular
weight. Advantageously, molecular weights
for the fluoro polymer of 8,000 or higher
are employed. As employed herein the term
105 "hydrophobic polymer" or "fluoro-polymer"
refers to polymers such as, e.g., polytetra-
fluoroethylene, noted above, which have crys-
talline melt temperatures above about 300°C.
and are sinterable at temperatures from 130

around their crystalline melt temperature to the decomposition temperature of the respective polymer. Suitable starting materials of this type include aqueous suspensions containing 60% by weight of polytetrafluoroethylene particles, for example those available under the trade names "Teflon" 30 and "Teflon" 41X ("Teflon" is a Registered Trade Mark). Such dispersions may contain compatible wetting agents which may be of cationic, non-ionic and anionic types. Where the polymeric dispersion contains such wetting or stabilizing agents, precipitation of the particulate polymer onto the surfaces of the cellulosic fibrous substrate or cellulosic fibrous substrate modified with colloidal mineral is facilitated by use of precipitating agents inducing the opposite charge upon the substrate particles.

The fibrous pore-forming substrate can be formed by any conventional mechanical and/or chemical pulp-forming procedure employed in the paper-making or like art. The fibrous pulp can be prepared from flax, cereal straws, wood products and like cellulosic pulp rendering starting materials. The degradation by mechanical and/or chemical means is continued until a fibrous pulp suspension is obtained having the requisite dimensional parameters. As the size of the pore structure in the ultimate sintered composition corresponds closely to the dimension of the volume occupied by the fibrous substrate prior to combustion thereof to form the gaseous product which exposes the volume to ambient atmosphere, the dimension of the fibrous substrate employed in compounding the sinterable stock will depend upon the use and characteristics desired of the ultimate porous membrane composition. By way of example, in the use of the sinterable stock to form a porous wettable membrane matrix for trapped electrolytes in gas-consuming fuel cells, a fibrous suspension wherein the individual fibers have an average cross section of from 0.5 to 20 microns and more advantageously from 1 to 5 microns is preferred. For other uses such as battery diaphragms and electrode supports, the fibers can have an average diameter of from 0.5 to 200 microns. The length of the fiber can vary, again being determined by its ultimate use. In general fibers having an average length of from 5 microns to 10 millimeters can be employed.

In a preferred embodiment of the invention, colloidal mineral components or other non-consumable and hydrophilic materials increasing the wettability of the hydrophilic fluoro-plastics are incorporated into the pore structure of the matrix by sorbing suitable colloidal minerals on fibrous cellulose prior to the deposition of the colloidal hydrophobic polymer to form the coagulum or aggregate. When the final structure is subjected to the sintering temperatures of the

fluoro-polymer the cellulosic material burns out leaving the wetting filler deposited in the pore structure previously occupied by the cellulosic material and now exposed to ambient atmosphere by the decomposition gases. The resulting structure is characterized by good mechanical strength, high porosity, selective wetting characteristics and excellent stability to chemical attack by the electrolytes. The electrolyte-stable aqueous wettable fillers function as "stepping stones" to permit the electrolyte to achieve a phase continuity over the surfaces defining the pores of the porous matrix between the electrodes. For optimum capillary requirements the electrolyte-stable wettable fillers should preferably have a particle size in the 0.01 to 0.2 micron range and be present in relation to the fluorocarbon polymer at a ratio of from 0.1 to 10.0 on a weight basis. Matrices particularly suitable will employ a particulate fluorocarbon polymer having an average particle size of from 0.1 to 50 microns, with the pores having an average diameter of from 0.5 to 10 microns and the colloidal mineral filler having an average particle size of from 0.01 to 0.2 microns. To have the most efficient electrolyte wetting, the mineral phase should be uniformly arranged from major surface to major surface of the matrix. Exemplary wettable fillers for filling the aforesaid capillary requirements include exploded silicon dioxide, potassium titanate, titanium dioxide, thoria and zirconia. Exploded silicon dioxide is a material obtained by heating silica containing some free water or water of hydration which causes the silica to be blown up as a very porous material. This material is crushed to provide silica particles which are very finely divided but still porous. The aforesaid wettable fillers may be in fibrous or powder form.

Having described the invention in general terms, to more particularly illustrate the invention a detailed working example will be set forth.

EXAMPLE

Twelve grams of ashless filter paper (no. 41 Watman), 250cc's of distilled water, and one cc of a 10% aqueous solution of trimethyl pelargonate ammonium hydrochloride, and 6 grams of colloidal silica, are charged to a Waring type blender and mixed for fifteen minutes at approximately three-quarters the rated capacity of the blender. Sixty grams of a 50% by volume aqueous dispersion of polytetrafluoroethylene, stabilized with a non-ionic surfactant, is added to 100cc's of distilled water and the mixture charged to the blender while the blender is turned on at 30% of the maximum speed. After all the dispersion has been added the resultant charge is agitated for an additional fifteen minutes. Thereafter, with the mixture subjected to a constant

speed, approximately 30% of the maximum blender speed, 150cc's of acetone are added and the mixture stirred for an additional five minutes.

- 5 The coagulated slurry is collected by filtration in a vacuum funnel and the resultant cake dried at 100°C. at 25 inches (Hg) of vacuum for sixteen hours. The resulting dried
- 10 cake is broken up in the blender until a loose, fluffy, fibrous product is obtained. Three grams of the resultant loose fibers and 150cc's of distilled water are mixed in the blender at high speed for one minute. Trapped
- 15 air is removed in a vacuum assembly. A 9 centimeter filter paper is placed on a vacuum funnel and the slurry deposited thereon. The slurry is allowed to settle slowly in the absence of a vacuum for approximately two
- 20 minutes and a vacuum then applied until water is no longer extractable. The upper surface can be rendered more even by pressing down upon the mat with a filter paper of the same size as below. The resulting
- 25 slurried cake is dried overnight at 150°F. The filter papers are removed and the mat placed in a muffle furnace at 670°F. for 15 minutes, or until all the cellulose is burned out. The mat is allowed to cool slowly at
- 30 room temperature and the resultant porous plastic sheet is placed in a hot nitric acid reflux assembly and boiled until the polymeric material achieves its characteristic off-white color. The matrix as prepared above
- 35 has excellent utility in a fuel cell for retaining an aqueous electrolyte, or as a support in electrode construction. In the electrode construction, one surface of a thin sheet of the matrix is coated with an activating
- 40 material such as platinum black and the polytetrafluoroethylene surface maintained in contact with fuel gas, with the activated surface being in contact with the electrolyte.

- 45 Additionally, in the Example, prior to the addition of the polymer dispersion, chemically stable wettable fillers such as exploded silicon dioxide, potassium titanate, titanium dioxide, thorium or zirconia, either in powder or fiber form, can be added to the fibrous suspension. The resultant product will be
- 50 similar to the product obtained in the example except that the inert filler will be present at the porous openings of the plastic matrix. This expediency permits the tailormaking of the matrix as to surface properties, such as wetting and the like.
- 55

- 60 Although the present invention has been described with emphasis being placed upon fuel cell applications, it is apparent, as noted in the preamble of the specification, that the described structures will have numerous applications as filters, diaphragms and the like. The hydrophobic polymer structures can be made having varying porosities and pore sizes, including membranes where the actual
- 65 porosity is not discernible, i.e., where it is

doubtful whether the pores are in the sub-micron range or are present as simple spaces between molecular chains. Since the pore size can be accurately determined, and because of the chemical inertness and heat resistant properties of the matrices, they can be used in numerous applications which will be apparent to one skilled in the art. Furthermore, according to the present invention it is possible to construct the novel matrix around a support such as a metal screen to improve its mechanical stability and render the matrix electrically conductive. The various modifications of the matrices and their numerous applications are to be included herein, with the invention only being limited by the appended claims.

WHAT WE CLAIM IS:—

1. A method for preparing porous shaped bodies comprising a hydrophobic polymeric matrix having preselected wettable characteristics, which method comprises the steps of precipitating a fluorocarbon polymer onto loose fibers having a charge opposite to that of said polymer to form a polymer-fiber aggregate, forming said aggregate into a desired shape, elevating said formed aggregate to a temperature at which said precipitated polymer will sinter, maintaining said aggregate at said temperature for a time sufficient to cause said polymer to sinter and form a pliable and coherent mass and consume said fibers, thus exposing the volume previously occupied by said consumable fibers to ambient atmosphere.
2. A method as claimed in claim 1, wherein said consumable fibers are a cellulosic material oxidizable to a carbon-containing gas at the sintering temperature of the fluorocarbon polymer.
3. A method as claimed in claim 1 or claim 2, wherein the fluorocarbon polymer is polytetrafluoroethylene.
4. A method as claimed in any of the preceding claims, wherein an aqueous, wettable, finely divided particulate mineral is adsorbed on the fibers before said fluorocarbon polymer is precipitated.
5. A method as claimed in claim 4, wherein said wettable mineral has a particle size from 0.01 to 0.2 microns.
6. A method as claimed in any of the preceding claims, comprising absorbing a cationic agent onto the surface of the cellulosic fibers before the hydrophobic polymer is precipitated.
7. A method as claimed in any of the preceding claims, wherein the cellulosic fibers have an average cross section of 0.5 to 20 microns and an average length from 5 microns to 10 millimeters.
8. A method as claimed in any of the preceding claims, wherein the ratio of polymer

to cellulosic fibers is from 0.1 to 10.0 on a weight basis.

- 5 9. A method as claimed in claims 5, 7 and 8, wherein the wettable mineral has a particle size of from 0.01 to 0.2 microns and is exploded silicon dioxide, potassium titanate, titanium dioxide, thoria or zirconia.

- 10 10. A method as claimed in any of the preceding claims, wherein the fluorocarbon polymer is in the colloidal state.

11. Porous bodies made by a method as claimed in any of the preceding claims.

- 15 12. A hydrophobic polymeric matrix having preselected wettable characteristics comprising a continuous phase of sintered fluorocarbon polymeric material having a series of integral interconnecting pores and a discontinuous colloidal mineral phase deposited in said pores, said mineral phase being uniformly arranged from major surface to major surface of said matrix.

- 20 13. A matrix as claimed in claim 12, wherein the particulate fluorocarbon polymer has an average particle size of from 0.1 to 50 microns and the pores have an average diameter of from 0.5 to 10 microns and said

colloidal mineral filler has an average particle size from 0.01 to 0.2 microns.

- 30 14. A matrix as claimed in claim 13, wherein the ratio of fluorocarbon polymer to colloidal mineral filler is from 0.1 to 10.0 on a weight basis.

- 35 15. A matrix as claimed in any one of claims 12 to 14, disposed as an element in an electrochemical cell comprising an anode, a cathode, and an electrolyte, said electrolyte separating said anode and cathode.

16. A matrix as claimed in claim 15, wherein the element is an electrolyte matrix.

- 40 17. A method of preparing a matrix substantially as set forth in the foregoing Example.

- 45 18. A method of preparing a matrix as claimed in claim 1, substantially as hereinbefore described.

19. A matrix prepared by the method as claimed in claim 17 or claim 18.

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DRAWINGS ATTACHED

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 (52) Index at acceptance

C1A Q3 Q4
 H1B F



(54) PROCESS FOR SEPARATING CARBONATE COMPOUNDS
 FROM THE ALKALINE ELECTROLYTES OF FUEL CELLS

- (71) We, VARTA AKTIENGESSELLSCHAFT, a German Company, of Neue Mainzer Strasse 54, Frankfurt am Main, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The invention relates to a process for separating carbonate compounds from the alkaline electrolytes of fuel cells.
- In fuel cells which are operated with oxygen from the air carbonate compounds are formed by reaction of the carbon dioxide of the air with metal electrolytes. These carbonate compounds have poor solubility and disturb the smooth functioning of the fuel cells by precipitating out.
- Carbonate compounds are also formed in large amounts/in fuel cells operated with hydrocarbon compounds, and with compounds such as methanol or ethanol.
- According to the invention there is provided a method of separating sodium carbonate and/or potassium carbonate from the alkaline electrolytes of fuel cells, which method comprises contacting the carbonate-containing liquid electrolyte over solid sodium hydroxide and/or solid potassium hydroxide.
- The liquid electrolyte, which is contaminated with carbonate, and which has also been diluted by the water formed in the chemical reactions occurring in the course of the operation of the fuel cell battery, is removed from the electrolyte space or from the electrolyte circuit of the fuel battery and is passed over the above-mentioned solid alkali hydroxide.
- The separation of the carbonate is based on the poor solubility of the alkali metal carbonates in saturated alkaline solutions.
- It is an advantage, in carrying out the method according to the invention, that the presence of methanol hardly affects the solubility, and precipitation of the carbonate can therefore be carried out in the presence of the liquid electrolyte which contains an appreciable amount of methanol.
- If, for example, the mixture of electrolyte and fuel, which has been derived from a methanol/air fuel battery and which is contaminated with potassium carbonate and reaction water, is passed over solid potassium hydroxide, then the potassium carbonate contained in the electrolyte will be almost completely separated out. For each mole of separated carbonate 2 moles of water of crystallisation are also separated.
- A carbonate-free saturated potassium hydroxide solution, mixed with methanol, then leaves the vessel below the solid hydroxide. This saturated potassium hydroxide solution may be mixed, in a mixing tank, with a further amount of methanol and water so as to adjust to a required concentration of the electrolyte; the resultant solution will then be returned into the electrolyte circuit.
- In an apparatus for carrying out the method according to the invention the electrolyte circuit is connectable to a storage vessel for storing solid alkali metal hydroxide; this connection can be established, when required and by means of an automatic control device or by hand, after which the content of alkali metal carbonate in the liquid electrolyte from the fuel cell exceeds a predetermined limit value. A saturated solution of the alkali metal hydroxide, which is practically free of carbonate, leaves the storage vessel. The saturated solution can be directly fed to the electrolyte space of the fuel cell. In a preferred form of construction of the apparatus for use in the method of the invention, the outlet of the storage vessel is connected to a mixing vessel for mixing together fuels and water.
- The solid alkali metal hydroxide may be mixed with Raschig rings or other filler substances, which cause the solid alkali (hydroxide) to be broken up, and thus result

in a better flow-through of the liquid electrolyte.

The drawing illustrates an apparatus for carrying out the method according to the invention in a methanol/oxygen fuel battery.

5 The solid alkali metal hydroxide, which may for example consist of solid potassium hydroxide, is located in the container 1, above the screen-like floor, or base, 2. In
10 the course of operation of the fuel battery, water is first of all passed from the storage container 3 and through valve 4 on to the solid alkali metal hydroxide this process is continued until a sufficient quantity of saturated hydroxide solution has accumulated in
15 the space 5 lying under the screen-like base or floor 2, this saturated hydroxide solution then being passed to the mixer 7 by way of valve 6. Water and methanol are fed into
20 the mixer 7 from containers 3 and 8 respectively and by way of valves 9 and 10 respectively, so that a mixture of fuel and electrolyte is formed which is in the proportions of 8 moles alkali hydroxide: 4 moles of
25 methanol: and 37.2 moles of water.

The mixture passes from the mixer 7 and through valve 11 into the storage container 12 from which this mixture is passed into the electrolyte space of the fuel battery 13.
30 In battery 13 the methanol is electrochemically decomposed with the accompanying formation of alkali metal carbonate. The liquid electrolyte leaving the fuel battery is passed to the storage container 12 by way
35 of valve 14: in this storage container 12 the liquid electrolyte is mixed with the liquid already present in the storage container 12. If the mixture in the storage container 12 contains, for each four mols of alkali
40 hydroxide, less than 2 mols of methanol or more than 43.3 mols of water or more than 2 mols of alkali carbonate, then valve 14 is closed by a suitable control circuit, valves 15 and 16 are opened, and part of the liquid
45 electrolyte contained in the storage container 12 is passed on to the solid alkali metal hydroxide. Subsequently and if necessary, any required further amount of methanol may be added to the mixer 7 from container
50 8; similarly, any further required amount of water may at this later stage be fed into the mixer 7 from the container 3. At the same

time a corresponding amount of fresh electrolyte/fuel mixture is fed to the storage container 12 from the mixer 7.

55 In the container 1 there is, relative to the amount of carbon dioxide which is evolved in the fuel cell 13 in the course of the complete decomposition of the methanol, an excess of solid alkali metal hydroxide, so that it is
60 ensured that separation of the carbonate will continue until all the methanol has been decomposed.

If oxygen from the air is used for the oxygen electrodes of the fuel battery, the stored amount of solid alkali hydroxide must be so controlled that the alkali carbonate formed by the carbon dioxide content in the air can also be separated.

65 The fuel cell 13 shown in the drawing is supplied with oxygen by decomposing a 30% strength aqueous solution of hydrogen peroxide, which is fed from the storage container 17 and is decomposed to oxygen and water in the reaction vessel 18. The gaseous
70 oxygen is passed to the oxygen electrodes of battery 13 by way of pipe 19. The water can be passed from the reaction vessel 18 into the storage container 3.

WHAT WE CLAIM IS:—

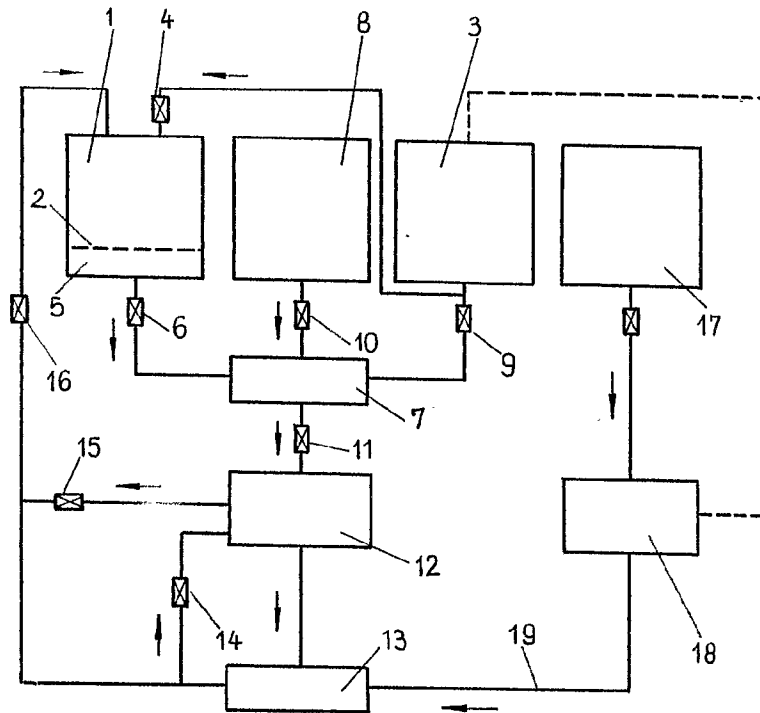
80 1. Method for separating sodium carbonate and/or potassium carbonate from alkaline electrolyte of fuel cells, which method comprises contacting the carbonate-containing liquid electrolyte with solid sodium hydroxide
85 and/or solid potassium hydroxide.

2. A method according to claim 1, in which the electrolyte passes directly from the fuel cell through a conduit, into a storage vessel containing the solid alkali metal hydroxide.

90 3. A method according to claim 2, wherein the electrolyte, after leaving the storage vessel, is mixed with water and fuel for the fuel cell, before passing back into the electrolyte chamber of the fuel cell.

95 4. A method according to claim 1 and substantially as described with reference to and as illustrated by the drawing.

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DRAWINGS ATTACHED

- (21) Application No. 9232/68 (22) Filed 26 Feb. 1968
 (31) Convention Application No. 2737 (32) Filed 24 Feb. 1967 in
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 (45) Complete Specification published 3 Feb. 1971
 (51) International Classification H 01 m 27/12
 (52) Index at acceptance H1B F



(54) IMPROVEMENTS IN OR RELATING TO FUEL CELLS
 HAVING AN AUTOMATIC CONTINUOUSLY
 DECARBONATED BASIC ELECTROLYTE

- (71) We, SOCIETE GENERALE DE CON-
 STRUCTIONS ELECTRIQUES ET MECANQUES
 (ALSTHOM), a French Body Corporate, of 38,
 Avenue Kleber, Paris 16°, France, do hereby
 5 declare the invention, for which we pray that
 a patent may be granted to us, and the
 method by which it is to be performed, to
 be particularly described in and by the
 following statement:—
- 10 It is well known that the problem of car-
 bonation of the basic electrolyte of a fuel
 cell is one of the most serious encountered
 heretofore in the effort to introduce fuel cells
 into industry.
- 15 In a fuel cell intended for industrial
 applications, which consumes the oxygen con-
 tained in the air, directly or indirectly, or a
 carbonaceous fuel carbonic acid is introduced
 into the cell from different sources. For
 20 example, air contains a certain proportion of
 carbon dioxide; the direct use of a car-
 bonaceous fuel gives carbonic acid as a
 product of reaction; and the reforming of a
 carbonaceous fuel produces hydrogen which,
 25 if its cost is to be kept at an acceptable level,
 i.e. if it has not been extensively purified,
 will contain a notable proportion of carbon
 dioxide.
- 30 If an acid medium is used, there are no
 problems in this respect, but it is well known
 that the choice of electrode materials then
 becomes restricted and that, of the various
 electrode catalysts, only the platinoids have
 35 so far enabled the development stage to be
 reached. An acid medium therefore results
 in a costly cell, the manufacture of which
 would in any case be restricted on account of
 the limited production of platinoids.
- 40 In a basic medium, on the other hand,
 many inexpensive and readily available
 materials can be used as electrodes or cata-
 lysts, both for the oxygen and for numerous
 fuels. For instance, oxygen produces a revers-
 45 ible reduction to perhydroxyl ions on many
 materials (silver, active carbon, etc.). In-
 expensive carbonaceous fuels like methanol
 react satisfactorily at low temperatures on
 such catalysts as nickel boride. But the
 carbonic acid produced soon carbonates the
 basic electrolyte and ultimately transforms it
 completely into an acid carbonate solution,
 which in the case of most cells results in a
 great decay in performance.
- 50 Naturally, endeavours have been made for
 a long time to find ways and means of con-
 tinuously or intermittently decarbonating the
 electrolyte. Many of these processes require
 more energy than the cell produces, and some
 call for auxiliary reactants and certain
 ancillary devices. One of the most satisfactory
 methods consists of continuously or inter-
 mittently adding a base such as lime, which
 causes the formation of an insoluble carbonate.
 But apart from the need to ensure proper
 injection of the lime and filtration of the
 calcium carbonate, this method calls for stor-
 ing lime in addition to fuel in a proportion
 of 1.75 kg of lime for 1 kg of methanol,
 and also requires complex and bulky
 ancillary equipment.
- 55 A method proposed by Justi (Journal of
 the Electrochemical Society, 1961, vol. 108,
 11, 1073) consists of associating with the
 cell proper an electrolysis cell whose anode
 and cathode compartments are separated by
 a cationic diaphragm. If an adequate voltage
 is applied across the two electrodes of this
 electrolysis cell, the K⁺ cations of the car-
 bonated potassium solution extracted from the
 fuel cell and introduced into the electrolysis
 cell will pass through the diaphragm in re-
 sponse to the electrical field, at the same
 time as oxygen and carbon dioxide is
 given off at the anode and hydrogen is given
 off at the cathode. In other words, an electro-
 dialysis is effected that transforms the car-
 bonate of potassium solution into potash, but
 to the energy required for this transformation
 must be added the energy for electrolysis of
 the water. This additional expenditure of
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[Price 5s. 0d. (25p)]

energy must be avoided either by consuming the hydrogen and oxygen produced in an auxiliary cell, or by using two identical reversible electrodes and periodically reversing their functions. In any event, this process entails losses due to the excess voltages at the electrodes and to the fall in ohmic resistance in the electrodialysis cell, as well as possible similar losses in the auxiliary cell. Moreover, the electrodialysis cell and possibly also the auxiliary cell represent additional items of equipment distinct from the fuel cell proper.

In point of fact, none of the methods considered or tried out up to now have proved really satisfactory. Notwithstanding all the advantages adhering to a basic medium, the absence of a suitable decarbonating method has compelled many research teams to turn towards acid electrolyte cells (with the concomitant problem of replacing the platinoids), towards neutral media (with their present very poor performance), or towards indirect hydrogen cells (which require purification of the hydrogen produced by reforming a carbonated fuel).

It is an object of the present invention to provide a basic electrolyte cell capable of automatically eliminating the carbonic acid introduced from any source whatsoever, without a notable expenditure of energy other than that resulting from the normal polarizations of the cell and without any ancillary equipment, thereby enabling all the advantages of alkaline media to be retained without their attendant drawbacks.

The present invention is based on the fact that, in a fuel cell divided into two half-cells by a semi-permeable diaphragm, the development of the electrochemical reactions at the electrodes results in the two electrolyte solutions being rendered mutually heterogeneous.

Considering, for example, the case of such a cell consuming hydrogen and oxygen, the oxygen reduction will produce OH^- ions in the proportion of one ion for each electron exchanged, while the hydrogen oxidation will consume OH^- ions in the proportion of one ion for each electron exchanged. But because the diaphragm prevents the transit of OH^- ions from one compartment to the other by convection, such transit is, for all practical purposes, possible only by migration in response to the electrical field (diffusion as a result of the concentration gradient being as a rule virtually negligible). But if a non-anionic diaphragm is chosen, i.e. one which is either cationic or non-ionic, the transport number of the OH^- ions through the diaphragm will be less than unity. Hence no compensation takes place, and, as the reactions proceed, the electrolyte of the cathode compartment is base-enriched and the electrolyte of the anode compartment is base-

impoverished. If, instead of pure hydrogen, recourse were had to hydrogen containing carbon dioxide produced by a reforming, or to a carbonaceous fuel like methanol, the additional OH^- ions consumed by the carbonic acid present or produced will impoverish the electrolyte of the anode compartment more rapidly still than in the case of pure hydrogen. If this heterogeneous-going trend is pursued, the cathode-compartment solution will have its base-normality increased, which will substantially affect neither the pH-value nor the oxygen reducing conditions, which will remain just as favourable. In contrast, the anode-compartment solution will have its pH-value reduced, and this reduction can be allowed to proceed to the point where carbon dioxide begins to be liberated, i.e. in practice with moderately concentrated electrolyte solutions, down to a pH-value of the order of 10 to 9. Now, whereas the performance of an oxygen electrode at such a pH-value would as a rule be very poor, it is well known that that of an electrode using a fuel such as methanol remains virtually unchanged up to a pH-value of 14 to 15, as extensive experimental work has shown. So far as the stability of a catalyst like nickel boride is concerned, it is even greater in such a near-neutral medium than in a concentrated potash medium.

The invention consists in a method of producing electric current by means of a fuel cell with automatic continuously decarbonated basic electrolyte, said cell being divided by a semi-permeable diaphragm into two compartments, anodic and cathodic, an electrolyte flowing parallel to the semi-permeable diaphragm passing through each of these compartments, wherein said diaphragm is non-anionic, the output of the electrolytes is regulated so that the solution having passed through the anode compartment reaches the pH-value at which the carbon dioxide is released in gaseous form, the gaseous carbon dioxide is effectively separated from the electrolyte at the outlet of the anode compartment and after this separation, the two electrolytes are mixed, then split up once more into two similar fractions and reintroduced into the cell to recommence the cycle.

The small magnitude of the convection movement of the electrolyte in the direction of flow due to the speed of flow of the electrolyte avoids any re-homogenization of the electrolyte in the two electrolyte compartments.

If the diaphragm is microporous and non-ionic, it is preferable for the electrolyte to contain, in addition to the base, a notable concentration of an indifferent salt such as a salt of the base considered, and of a non-electroactive anion acid. An indifferent salt is one which does not react on the elec-

trodes, e.g. one of which neither the anion nor cation is electro-active.

5 The fuel cell is preferably divided into a plurality of discrete elementary cells through which the electrolyte flows successively, the anodic electrolyte in each cell being of substantially uniform pH.

10 The fuel cell at each cycle eliminates a quantity of carbon dioxide equal to the quantity that has found its way in, in some form or other, during the cycle. Subordinating the electrolyte throughputs to the current load or to the pH-value of the solution on exit from the anode compartment ensures 15 that this quantity of gas is liberated. Under steady-state conditions, the electrolyte, subsequent to re-homogenization, will be a solution containing the initial base, neutral carbonate of this base, and possibly also the indifferent salt referred to above.

20 The addition of an indifferent salt in the case of a non-ionic diaphragm is intended to maintain the OH⁻ transport number as constant as possible. Indeed, unless this addition is made, the transport number of the OH⁻ ions in relation to the K⁺ or Na⁺ ions 25 would tend to increase as the electrolytes progressed, because of the heterogenization of the concentrations. The addition of a considerable concentration of an indifferent salt, equal to many times that of the base, tends to maintain the transport number of the OH⁻ ions substantially constant throughout the transit, thus obviating the need to increase 30 unnecessarily the extent of the discrete cell or cells of low pH-value to that of high pH-value.

35 The fuel cell is divided into discrete elementary cells so that the electrodes can operate most efficiently. In an undivided cell the pH will vary in the anode compartment from the electrolyte inlet to the outlet and as the electrode can only operate most efficiently over a narrow pH range, it must 40 operate inefficiently at one end or other. By dividing the cell into a plurality of elements the electrolyte in each cell is of substantially uniform pH.

45 When the cell is subdivided into discrete elements, it is desirable that each elementary cell contributes the same fraction of the total current. One way of ensuring this is to construct a multiple cell of the type described above in which the minimum possible number 50 of elements is used; to determine the fraction of the total current provided by each cell in the multiple cell; to calculate the lowest common denominator of these fractions and to construct a second multiple cell in which 55 the number of elementary cells is equal to this lowest common denominator and each cell contributes the same fraction of the total current.

60 The single figure of the accompanying drawing illustrates the case of a methanol-

air cell in which the advance of the anode electrolyte through the cell is divided into three regions of homogeneous pH-value, of which the first covers three-quarters of the total current, the second one-eighth of the total current, and the third one-eighth of the total current also. The complete fuel cell is thus divided into eight unit cells 1 which are series-connected electrically by means of 70 electrical connections schematized by reference numeral 2. In order to reduce the height of the drawing, only four of the first six unit cells are shown. These unit cells are each divided by a semi-permeable diaphragm into two thin compartments a few millimetres thick, to wit an anode compartment 4 and a cathode compartment 5. The anode electrolyte is delivered through a conduit 6, is driven by a pump 7, receives at 8 an injection of methanol from an upper tank (not shown), and transits in succession through the anode compartment 4 of each of the eight unit cells 1. On exit from the set of cells, subsequent to liberation of carbon dioxide at 9 from a tank 10, the anode electrolyte reaching the conduit 11 is mixed in conduit 12 with the electrolyte issuing through 80 conduit 13 from the cathode compartments 5. From conduit 12 part of the electrolyte passes into conduit 6 and part into a conduit 14 which, subsequent to the drive imparted by a pump 15, feeds the cathode compartments 5 of the eight unit cells 1 in succession.

The cathode compartment of each cell 1 contains a meshed electrode 16 adapted to receive air to be emulsified directly into the electrolyte. The air to be emulsified is supplied by compressors (not shown) and is delivered through conduits 18 into the cathode compartment 5.

105 The electrolyte throughput can be adjusted by means of the pumps 7 and 15. Through the agency of suitable means (not shown, since they fall outside the scope of the present invention and can be of any convenient type), this throughput can be controlled in response to the pH-value of the electrolyte solution on exit from the anode compartments 4, in the tank 10, or to the electric current delivered by the fuel cell.

115 It will therefore be clear that the decarbonating method used in the present invention is tantamount to a cyclic evolution of the electrolyte but that the normal electrochemical processes in the cell effect the required transformation of the electrolyte themselves. Therefore, insofar as the fuel oxidation energy up to the CO₂ stage is concerned, there is no loss of energy other than that involved in the normal polarizations of the cell. Nor is there any ancillary item of equipment other than the normal ones associated with the fuel cell.

WHAT WE CLAIM IS:—

1. A method of producing electric current 130

- by means of a fuel cell with automatic continuously decarbonated basic electrolyte, said cell being divided by a semi-permeable diaphragm into two compartments, anodic and cathodic, an electrolyte flowing parallel to the semi-permeable diaphragm passing through each of these compartments, wherein said diaphragm is non-anionic, the output of the electrolytes is regulated so that the solution having passed through the anode compartment reaches the pH-value at which the carbon dioxide is released in gaseous form, the gaseous carbon dioxide is effectively separated from the electrolyte at the outlet of the anode compartment and after this separation, the two electrolytes are mixed, then split up once more into two similar fractions and reintroduced into the cell to recommence the cycle.
- 20 2. A method as claimed in claim 1, in which the diaphragm is non-ionic and the electrolyte contains, in addition to a base, a

concentration of an indifferent salt which is large relative to the concentration of the base.

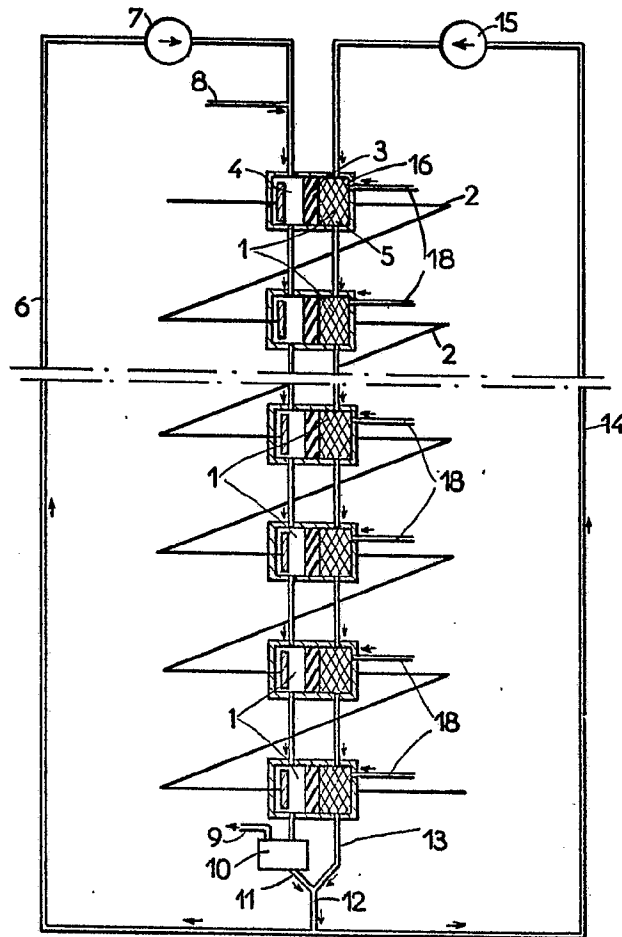
3. A method as claimed in claim 1 in which the cell is a multiple cell comprising a plurality of discrete elementary cells through which the electrolyte flows successively, the anodic electrolyte in each cell being of substantially uniform pH.

4. A method as claimed in claim 3 in which the discrete elementary cells are joined in series and each provides an equal fraction of the total current of the multiple cell.

5. A method of producing electric current by means of a fuel cell substantially as hereinbefore described with reference to the accompanying drawing.

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DRAWINGS ATTACHED

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 (51) International Classification H 01 m 27/00
 (52) Index at acceptance

H1B F
 G3R 1B 21B3 70



(54) THE USE OF LIQUID REACTANTS IN FUEL CELLS

(71) We, SIEMENS AKTIENGESellschaft, a Germany Company, of Berlin and Munich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

In fuel cells operated with liquid reactants dissolved in the electrolytes, the metering of the reactants is more difficult than in fuel cells operated with gaseous fuels and oxidants, in which the fuel, for example hydrogen, and the oxidant, for example oxygen, may be fed to the fuel cells under constant pressure. In the case of a fuel cell operating with liquid fuel, for example hydrazine, or liquid oxidant, for example hydrogen peroxide, the liquid reactant may be added to the electrolyte either continuously or discontinuously. While the concentration of the liquid reactant in the electrolyte can be kept constant when the liquid reactant is continuously added, the concentration will vary from time to time when the reactant is discontinuously added.

If fuel cells are operated under variable conditions, for example under a fluctuating load and fluctuating temperature, the fuels cells do not operate under optimum conditions when the concentration of the liquid reactant is maintained constant, because for an optimum operation of the fuel cells the concentration must always be adapted to the temperature and load fluctuations. If the concentration of the liquid reactant in such a cell is too high, the danger exists, above all, that the counter-electrode will be unfavourably influenced and that the potential of this electrode will be reduced or will even collapse. On the other hand, too low a concentration results in an impairment of the electrodes.

According to one aspect of the present invention there is provided in combination a fuel cell, means for delivering liquid reactant into the electrolyte of the fuel cell, and an

electrical controller connected between the cell and the said means and operative, when the fuel cell is operating in a concentration range such that an increase in concentration of the liquid reactant in the cell electrolyte results in an increase of the cell voltage with a given load, to effect an increase in the delivery rate of the said means when the cell voltage decreases and to effect a decrease in the delivery rate when the cell voltage increases.

According to a second aspect of the present invention there is provided a method of operating a fuel cell, wherein liquid reactant is delivered into the electrolyte of the cell, the concentration of liquid reactant in the electrolyte is maintained in a range such that an increase in that concentration results in an increase of the cell voltage with a given load, and an electrical controller is arranged to operate in dependence upon the cell voltage so as to effect an increase in the rate of delivery of liquid reactant into the electrolyte when the cell voltage decreases and to effect a decrease in the delivery rate when the cell voltage increases.

In one application of the invention the cell voltage so control, through the controller, the motor of a metering pump for the liquid reactant that the delivery rate of the pump is increased when the cell voltage falls and is reduced when the cell voltage rises, the fuel cell operating in a concentration range such that an increase in the concentration of the liquid reactant results in an increase of the cell voltage with equal load.

The invention is particularly suitable for the operation of fuel cells in which hydrazine in solution in alkaline electrolyte is employed. However, other substances such as methanol, a boronate (it will be appreciated that this term embraces compounds of the general formula XBH_4 , where X is an alkali metal), or hydrogen peroxide, may be employed as liquid reactants.

When the invention is applied to a fuel

cell operated with 6 n KOH and hydrazine, the concentration range with which an increase in the concentration of the hydrazine results in an increase of the cell voltage for a given load is about 0.01 mol to 2 mol per litre 6 n KOH, provided that oxygen is employed as the oxidant. If the loading of the fuel cell is increased, the cell voltage falls, whereupon the quantity of hydrazine delivered should be increased to such an extent that the voltage set at the controller is maintained. This can obviate the need for any additional electronic device to maintain the voltage constant.

By application of the invention over-metering of the liquid reactant, and thus an impairment of the counter-electrode, can be avoided. Moreover, losses due to chemical short-circuiting and to spontaneous decomposition of hydrazine when used as the liquid reactant can be reduced.

Reference will now be made, by way of example, to the accompanying drawing, in which:

Figure 1 is a schematic diagram of a combination of apparatus employed in one embodiment of the present invention;

Figure 2 is a diagram of controller circuitry that may be used in the apparatus of Figure 1; and

Figure 3 shows diagrammatically a vertical section through a fuel cell.

In Figure 1, there is denoted by 1 a fuel cell whose electrolyte chamber is connected with an electrolyte supply vessel 5 by pipes 2 and 3 and a pump 4. A supply vessel for the fuel or the oxidant is denoted by 6. The liquid reactant from the vessel 6 is fed by a pump 7 through a pipe 8 into the electrolyte circuit at 13. An electric motor 9 which drives the metering pump 7 is electrically connected to an electrical controller 10. Electric conductors extend from the various electrodes of the fuel cell to the controller 10 and to a driving motor 11 of the pump 4. A load connected to the fuel cell is denoted by 12.

When the cell voltage falls below a preset value, the driving current of the motor 9 is increased by the controller 10, giving a consequent increase in the quantity of liquid reactant fed into the electrolyte circuit at 13. Consequently the cell voltage is increased, with the result that the driving current of the motor 9 is reduced by means of the controller. Thus the delivery rate of the pump 7 is reduced.

The motor 11 driving the pump 4 provided for the circulation of the electrolyte has the cell voltage applied to it, but could alternatively be operated independently of the cell voltage.

The controller 10 shown in Figure 1, which serves to control the pump motor 9, may be adapted to a plurality of fuel cells and to

their cell voltage or battery voltage. In the case of fuel batteries in which a relatively large number of individual cells are connected in series, a sufficiently high unidirectional voltage is available to enable normal amplifiers to be employed. In this case, the motor 9 of the pump 7 will be controlled by means of a comparison between the actual and desired values.

Figure 2 illustrates the construction of a controller 10 which may be employed for an individual cell or small battery. The lowest voltage at which the controller can operate is 0.5 V. In this controller, the threshold value of a transistor 14 is utilised as the desired value for the regulation. When the cell voltage decreases, the actual value, which is an optimum proportion of the cell voltage and is tapped at a 100-ohm resistor 15, decreases. When this actual value falls below the threshold value of the transistor 14, this transistor acquires a high ohmic value, becoming non-conductive. Consequently, a transistor 16 also acquires a high ohmic value and a transistor 17 a low ohmic value. Current can then flow through the transistor 17 to a motor 18 (which may be the motor 9 of Figure 1) used to drive the liquid reactant metering pump. When the cell voltage increases, the action is reversed and the transistors 14 and 16 acquire low ohmic value. The transistor 17 acquires high ohmic value and the supply of current to the motor 18 is thus blocked and the delivery of reactant is stopped. The point at which the motor is to start may be set by means of the tap on the 100-ohm resistor 15.

Figure 3 diagrammatically illustrates a fuel cell which may be operated, in an embodiment of the invention, with liquid hydrazine and gaseous oxygen. The anode consists of a platinised nicked gauze 19 and the cathode of pulverous Raney silver 20. There is denoted by 21 an asbestos diaphragm, by 22 a fine-meshed wire gauze, and by 23 a coarse-meshed wire gauge. The hydrazine-containing electrolyte is fed into the asbestos fibre layer at 24. At a preset cell voltage of 0.73 V, the following hydrazine concentrations are set up in this fuel cell as a function of the load: at 5 mA/cm², the N₂H₄OH concentration is 0.03 to 0.05 mol, at 10 mA/cm² loading it is 0.1 mol, and at 15 mA/cm² it is 0.25 mol.

WHAT WE CLAIM IS:—

1. In combination a fuel cell, means for delivering liquid reactant into the electrolyte of the fuel cell, and an electrical controller connected between the cell and the said means and operative, when the fuel cell is operating in a concentration range such that an increase in concentration of liquid reactant in the cell electrolyte results in an increase of the cell voltage with a given load, to effect an increase in the delivery rate of the

said means when the cell voltage decreases and to effect a decrease in the delivery rate when the cell voltage increases.

5 2. A combination as claimed in claim 1, wherein the said means are arranged to deliver the liquid reactant into the electrolyte continuously substantially throughout operation in the said concentration range.

10 3. A combination as claimed in claim 1 or 2, wherein the said means include a metering pump driven by an electric motor the speed of which is controlled by the said electrical controller.

15 4. A combination as claimed in claim 1, substantially as hereinbefore described with reference to Figure 1, with reference to Figures 1 and 2, with reference to Figures 1 and 3, or with reference to Figures 1 to 3 of the accompanying drawing.

20 5. A method of operating a fuel cell, wherein liquid reactant is delivered into the electrolyte of the cell, the concentration of liquid reactant in the electrolyte is maintained in a range such that an increase in that
25 concentration results in an increase of the cell voltage with a given load, and an electrical controller is arranged to operate in dependence upon the cell voltage so as to effect an increase in the rate of delivery of
30 liquid reactant into the electrolyte when the

cell voltage decreases and to effect a decrease in the delivery rate when the cell voltage increases.

6. A method as claimed in claim 5, wherein the delivery of the liquid reactant into the electrolyte is continuous substantially
35 throughout operation in the said range of concentrations.

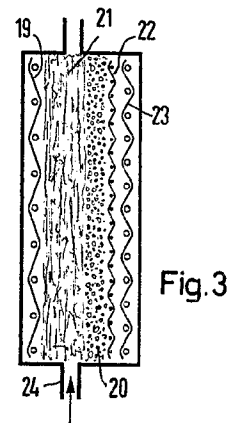
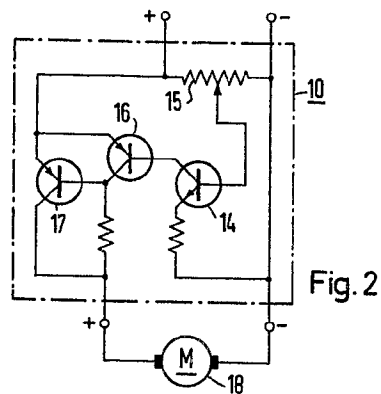
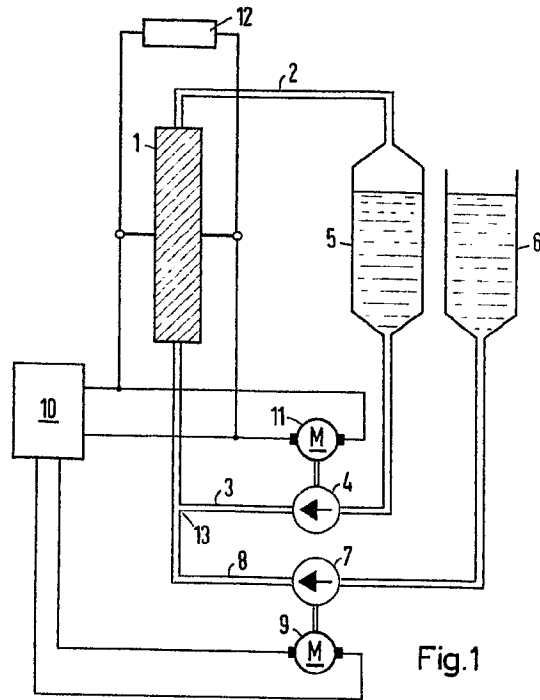
7. A method as claimed in claim 5 or 6, wherein the delivery of the liquid reactant into the electrolyte is effected by means of a metering pump driven by an electric motor the speed of which is controlled by the said electrical controller.

8. A method as claimed in claim 5, 6, or 7, wherein the liquid reactant comprises hydrazine, methanol, a boranate, or hydrogen peroxide.

9. A method of operating a fuel cell, substantially as hereinbefore described with reference to Figure 1, or with reference to
50 Figures 1 and 2, of the accompanying drawing.

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(54) SYSTEM FOR REGULATING A FUEL CELL UNIT

- (71) We, ROBERT BOSCH GmbH, a German Company, of 4, Breitscheidstrasse, Stuttgart W, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to a system for regulating at any one time the operating condition of a unit comprising one or a plurality of electro-chemical fuel cells which are operated by fuel dissolved in the electrolyte and a gaseous oxidizing agent.
- It is known to control the temperature in a hydrogen/oxygen fuel cell in conjunction with a hydrogen generator by cooling the electrolyte by the hydrogen fed to the cell and to flush the cells with hydrogen at specific intervals of time in order to remove impurities.
- It is also known to control the power output and the output voltages in a hydrogen/oxygen fuel cell.
- These methods have the disadvantage that only some of the operating parameters which have to be observed for the continuous operation of a fuel cell under optimum conditions, are measured and used for the purpose of control, so that a permanently high power output is not ensured for the continuous operation of such a cell.
- The present invention provides a system which enables a fuel cell unit to be operated permanently under optimum operating conditions and which enables the maximum power to be taken from the said unit at all times.
- In accordance with the present invention there is provided a system for regulating the operating condition of a unit comprising at least one electro-chemical fuel cell which is operated by fuel dissolved in the electrolyte and a gaseous oxidising agent, electrical signals characteristic of the electrode potential of the cell, the temperature of the cell, and the terminal voltage and current of the unit being transmitted to an electronic control device, the terminal voltage and current of the unit being used by the control device to derive a signal representative of the power output of the unit, all the signals enabling the electronic control device to regulate each of a plurality of regulating processes for maintaining the operation of the unit at its optimum condition, the first regulating process being the intermittent supply of a mixture of fuel and electrolyte to the cell when the working temperature is exceeded, the supply of fuel and electrolyte maintaining the temperature at or about the optimum value, the second regulating process being the intermittent supply of a mixture of fuel and electrolyte to the cell when the electrode potential of the cell drops below a preset limiting value, the third regulating process being the supplying of a mixture of fuel and electrolyte to the cell by the action of an electronic time switch element in time intervals which are controlled in dependence upon the power output, the third regulating process only being operative if processes one or two have not occurred, a fourth regulating process being the opening of an oxygen outlet valve by the action of the electronic time switch element in time intervals controlled by the power output and/or electrode potential of the cell, the electrode of the cell being rinsed in a stream of oxygen, and a fifth regulating process whereby the terminal output voltage is kept constantly at a fixed value independently of the power output, the electronic control device also serves to switch on a limiting resistor when the power output from the unit exceeds a predetermined value, the limiting resistor serving to prevent the cell from becoming overloaded, and an electronically regulated load circuit is also provided for rapidly heating the cell to its optimum working temperature.
- To prevent current flowing from a cell producing a high voltage into a cell of lower voltage when a plurality of parallel-connected

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cells are used, the cells are decoupled by interposing an electrical network, two diodes in the simplest case, or by connecting the cells in control circuits which are isolated from each other.

The potentials of specially prepared and thus especially sensitive individual cells are used as measured potentials. The high sensitivity of these cells is attained by reducing the catalyst content of the electrodes to about 40% of the quantity customary in working electrodes.

The invention will now be described further by way of example, with reference to the accompanying drawings, in which:—

Fig. 1 is a block diagram of a fuel cell unit, and

Fig. 2 is a block circuit diagram of an electronic control device and the elements controlled thereby.

Referring to Fig. 1, a fuel cell unit comprises two fuel cells 1, an electronic control device 2, an oxygen bottle 3, a fuel/electrolyte reservoir 4, and electrolyte pumps 5. Temperature sensors and specially prepared individual cells whose potentials are used for measuring electrode potentials of the fuel cells are fitted into the fuel cells, 1, and are connected to the control device 2 by leads 6 and 7. Furthermore, the current supply leads 8 lead from the cells 1 to the control device 2 by way of diodes 9. Leads 10 lead outwardly from the control device 2 by way of an ammeter 11 and a voltmeter 12 to the connection terminals for tapping the working voltage. The terminal voltage and current of the unit as sensed by the voltmeter 12 and the ammeter 11 is used by the control device 2 to derive a signal representative of power output. A gas line 13 leads from the oxygen bottle 3 by way of a precision control valve 14 and a manometer 15 into the cells 1 and then into the fuel/electrolyte reservoir 4 by way of an oxygen outlet valve 16. A conduit 17 leads from the reservoir 4 by way of the electrolyte pumps 5 to the cells 1 and from there back into the reservoir 4. The oxygen outlet valve 16 and the electrolyte pumps 5 are controlled by the electronic control device 2 by way of electrical leads 18 and 19 and are supplied with current which is produced by the fuel cells 1 themselves.

To put the unit into operation, the oxygen bottle 3 is filled and is connected to the supply line 13. A fuel/electrolyte mixture comprising 4 kilogrammes potassium hydroxide and 1.5 litres methanol is made up to 12 litres with distilled water and filled into the fuel/electrolyte reservoir 4. Such a charge is adequate for 24 hours continuous operation at full load, and for a correspondingly longer time at part load. The main valve and the pressure-reducing valve of the oxygen bottle are now opened successively and an oxygen

excess pressure of 0.2 atmospheres, readable on the manometer 15, is set by means of the precision control valve 14. An output stage switch 20 (Fig. 2) is now switched to the desired output, for example 100 watts. As may be seen from Fig. 2, the switch 20 acts upon the temperature controller 21 by setting a nominal temperature value (70°C in this case) corresponding to this output. An "ON" button fitted into the front panel of the controller is now pressed, and the volt meter 12 indicates voltage. To flush the cells and to check that the electrolyte pumps 5 are operating satisfactorily, the pumps are actuated manually for a short time by pressing a button "ELECTROLYTE". To blow out any liquid which has accumulated in the gas line 13, the oxygen outlet valve 16 is actuated several times by pressing a button "OXYGEN". The fuel cell unit supplies sufficient current at room temperature to operate the two electrically operated devices 5 and 16.

If it is desired to attain the operating temperature as rapidly as possible, the voltage switch 23 is switched to the 10 volts stage. The cells are thereby loaded at a lower voltage and thus with a higher amperage by an internal electronically controlled load circuit 24 until the operating temperature is attained. A heating current controller 25 ensures that, in conjunction with the temperature controller 21, the maximum admissible amperage always sets in for the prevailing temperature. It is also possible to connect a load to the connection terminals during the heating-up operation. The load is then included in the load circuit, so that the electrical data of this circuit varies accordingly. The diodes 9 located in the current supply leads 8 between the fuel cells 1 and the control device 2, and the electrical decoupling of the parallel-connected cells achieved thereby, are provided for preventing current flowing from cells having a higher voltage into cells having a lower voltage, thus reducing the power of the unit, in the case where individual cells have, for whatever reason, lower voltages than the other cells.

When the operating temperature has been attained, as indicated by a pilot lamp going out, the voltage switch 23 is switched back to 12 volts and the full output can be tapped without further supervision of the unit, since the electronic controller now takes over all further operations. The output voltage is stabilized by a voltage regulator 26 which is known per se and which is in the form of a switching regulator. If the temperature exceeds the nominal value, the temperature controller 21 switches on the electrolyte pumps 5 for a specific interval of time which is controlled by an electronic time switching elements 27, so that cool liquid is metered from the fuel/electrolyte reservoir 4. A ratio of fuel to electrolyte is eventually obtained so that the fuel

content of the cell helps to maintain the temperature at its nominal value. However, if the power taken from the cells is too small, the joule heating produced is inadequate to maintain or exceed the nominal temperature and thus initiate a supply of fuel. The solution in the cells becomes deficient in fuel, so that satisfactory operation is no longer obtained. To supply the cells with fuel even in such cases, the electronic time switching element 27 is governed by the power output in such a manner that the electrolyte pumps 5 are switched on at specific intervals of time by way of the electronic time switching element 27 and fuel thus flows into the cells. However, if fuel-electrolyte mixture is fed to the cells by action of the temperature controller 21, the electronic time switching element 27 is switched into its corresponding condition with regard to this control task.

The temperature and power output are linked together very closely, the power output being dependent upon the temperature, i.e. each power output has an optimum working temperature. As is shown in Fig. 2, the temperature regulator 21 is controlled by the output stage switch 20, which enables specific output ranges to be adjusted (e.g. 0—50, 50—80, 80—100 watts). The higher the desired temperature at which the temperature regulator 21 switches on the fuel-electrolyte pump 5, so the higher the output range to which the stage switch 20 has to be adjusted. The temperature is measured by way of thermistors 22 which are incorporated in the fuel cells and are temperature dependent. A minimum value for the potentials of the individual cells is preset in the electronic control device, and when the potentials of the individual cells fall below this minimum value the fuel electrolyte pump is switched on. If no signal, which switches on the fuel-electrolyte pump, comes from either the temperature controller 21 or the individual cells, then no corresponding signal will be received by the electronic control device. Under these circumstances the electronic time switch element 27 maintains the fuel supply to the cells by switching on the fuel-electrolyte pump 5 at specific time intervals which are also in turn controlled by the power output.

As shown in Fig. 1 only one lead 19 passes from the electronic control device to the two electrolyte pumps 5. Thus the two parallel-connected cells are supplied by a respective fuel-electrolyte pump, both of these pumps being controlled in a parallel manner. It would therefore be just as possible to use only one pump having an appropriately larger output in the case shown in Fig. 1. It is possible for each fuel cell, where there is a plurality of parallel-connected cells, to have its own electronic control device. In this case, each pump would be controlled individually.

The oxygen outlet valve 16 is opened periodically to clean the gas space and the electrodes of electrolyte which has intruded and of foreign gases originating from the oxygen. The oxygen excess pressure is thereby relieved for 1 second and oxygen passes along the gas side of the electrodes and entrains any liquid film or gaseous impurities present on the electrodes. Furthermore, in this way, the three-phase limit (solid-liquid-gas) can set in the most reliable manner. Under normal operating conditions the oxygen outlet valve 16 is opened every 30 minutes by the electronic time switching element 27. However, if the power output of the unit is high, the oxygen outlet valve 16 can be controlled by, the power output and opened at an earlier instant. The electronic time switching element 27 is in this case also brought into its corresponding condition with regard to the opening of the valve 16, i.e. its condition 30 minutes before the valve 16 is due to be opened again.

The potentials of the built-in, specially sensitive measuring cells are continuously monitored by the electronic controller. If one or both of the potentials fall(s) below the preset value for examples 200 mV, a potential monitor 28 first of all initiates the opening of the oxygen outlet valve 16 and then initiates the supplying of fuel by switching on the electrolyte pumps 5. If these measures do not cause the potential to increase again, as might occur if there is a deficiency of fuel in the electrolyte supply or if no further oxygen is delivered, the load is isolated from the apparatus and the whole system for regulating the operation conditions of the cell units is switched off by way of a relay 29. The potential monitor 28 thereby serves as a last safety device, but is necessary for the continuous operation of the unit in order to protect the electrodes against damage.

If too high a power output is taken from the unit, a current limiting resistor 30 comes automatically into operation causing the resistor 30 to be connected in series with the load. The switching on of the resistor 30 prevents the cell from becoming overloaded.

If the temperature in a cell exceeds a limiting value detrimental to the electrodes, a built-in excess-temperature monitor 31 switches the whole system off by way of the relay 29. Too high a temperature can occur if, for example, one of the electrolyte pumps 5 fails, so that one of the cells is no longer cooled.

The described system of the present invention has the advantage that a fuel cell unit is regulated and controlled fully automatically to the extent where it can be operated for about 24 hours without supervision. When this period has expired, it is necessary merely to replace the fuel/electrolyte mixture and the oxygen bottle. No external source of cur-

rent is required to put the system into operation. If any faults occur during operation, the automatic control arrangement ensures that measures are taken to prevent damage to the electrodes of the individual cells. The unit can be put into operation again immediately after the faults have been rectified. A unit which operates in accordance with the present invention and which has a rated output of 100 watts at 65° to 70°C and a spatial requirement of 0.16 m³ is still easily transportable at a weight of 90 kilogrammes in the filled state.

WHAT WE CLAIM IS:—

1. A system for regulating the operating condition of a unit comprising at least one electro-chemical fuel cell which is operated by fuel dissolved in the electrolyte and a gaseous oxidising agent, electrical signals characteristic of the electrode potential of the cell, the temperature of the cell, and the terminal voltage and current of the unit being transmitted to an electronic control device, the terminal voltage and current of the unit being used by the control device to derive a signal representative of the power output of the unit, all the signals enabling the electronic control device to regulate each of a plurality of regulating processes for maintaining the operation of the unit at its optimum condition, the first regulating process being the intermittent supplying of a mixture of fuel and electrolyte to the cell when the working temperature is exceeded, the supply of fuel and electrolyte maintaining the temperature at or about the optimum value, the second regulating process being the intermittent supplying of a mixture of fuel and electrolyte to the cell when the electrode potential of the cell drops below a preset limiting value, the third regulating process being the supplying of a mixture of fuel and electrolyte to the cell by the action of an electronic time switch element in time intervals which are controlled in dependence upon the power output, the third regulating process only being operative if processes one or two have not occurred, a fourth regulating process being the opening of an oxygen outlet valve by the action of the electronic time

switch element in time intervals controlled by the power output and/or electrode potential of the cell, the electrodes of the cell being rinsed in a stream of oxygen, and a fifth regulating process whereby the terminal output voltage is kept constantly at a fixed value independently of the power output, the electronic control device also serves to switch on a limiting resistor when the power output from the unit exceeds a predetermined value, the limiting resistor serving to prevent the cell from becoming overloaded, and an electronically regulated load circuit is also provided for rapidly heating the cell to its optimum working temperature.

2. A system as claimed in claim 1 in which when a plurality of parallel-connected fuel cells are used, the fuel cells are electrically decoupled relative to each other.

3. A system as claimed in claim 1 in which when a plurality of parallel-connected fuel cells are used, each fuel cell has its own electronic control device.

4. A system as claimed in any of claims 1 to 3 in which specially prepared individual cells are fitted into the fuel cells, the potentials of the individual cells being used for measuring the electrode potentials of the fuel cells, the electrodes of the individual cells having a catalyst content smaller than that in the working electrodes of the fuel cell.

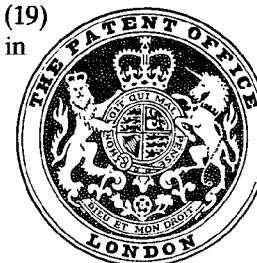
5. A system as claimed in any of claims 1 to 4 in which the electronic time switch element is switched into a condition simultaneously with the supply of fuel and electrolyte mixture to the fuel cell, the condition being such that the time switch element is at the beginning of a time interval after which it will cause the electrolyte pumps to be switched on again and the fuel and electrolyte mixture will flow into the fuel cell.

6. A system for regulating the operating conditions of a fuel cell unit constructed substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

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(54) FUEL CELL

(71) We, INSTITUT FRANCAIS DU PETROLE, a body corporate organised and existing under the laws of France, of 4 avenue de Bois-Preau, 92502 Rueil-Malmaison, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to fuel cells. A fuel cell usually comprises a block wherein electrodes delimit a plurality of chambers, some of these chambers containing a liquid or solid electrolyte, such as a solution of potassium hydroxide KOH, others being fed with a liquid fuel such as methanol or a gaseous fuel such as hydrogen gas of appropriate purity, and the remaining chambers being fed with a liquid or gaseous comburent (i.e. combustion-sustaining fluid) such as pure oxygen or air.

When the fuel cell is in operation and delivering electric power to a load circuit, the pressure in the various chambers is maintained at a determined value, either close to atmospheric pressure in one (most common) type of fuel cells, or much greater than atmospheric pressure in another, so-called high pressure, type of fuel cells.

When no electric power is delivered by the fuel cell to a load circuit, a certain residual rate of consumption of the reactants nevertheless occurs, owing to 'electrochemical short-circuit' within the fuel cell. In order to reduce this consumption, it is desirable to discontinue the feeding of reactants when the fuel cell is off duty.

When this is done, only the reactants contained in the fuel cell block at the time of switch-off can be consumed by electrochemical short-circuit. However, this consumption results in a pressure decrease in the chambers and the pressure differences which may appear between two chambers

separated by an electrode can result in a deterioration of the fuel cell by deformation of the electrodes.

Up to now different techniques have been used to obviate this drawback:-

(a) when the fuel cell is out of operation for only a short time interval, the feeding of the fuel cell with reactants may be not interrupted, and reactants continue to be consumed by electrochemical short-circuit within the fuel cell.

(b) when the fuel cell is out of operation for longer periods, the feeding of the fuel cell block may be interrupted and after the fuel and/or comburent chambers have been isolated, at least one liquid or gaseous auxiliary fluid at a determined pressure is introduced therein, this auxiliary fluid producing no electrochemical reactions.

Such a method has the drawback of requiring a special container to store a relatively large quantity of auxiliary fluid, thus increasing the weight and volume of the fuel assembly. Moreover the operator must perform additional operations to substitute the auxiliary fluid for the reactants and vice-versa, depending on whether the fuel cell is or not in operation.

It is desirable to provide a fuel cell wherein the pressure in at least some of the reactant chambers is automatically prevented from falling unduly, without requiring any intervention of the operator when the fuel cell is off duty.

According to the invention there is provided a fuel cell comprising a cell block having therein electrodes delimiting at least one first chamber for containing a comburent, and either at least one second chamber for containing a fuel and at least one third chamber for containing an electrolyte or at least one second chamber for containing a fuel-electrolyte mixture; inlet and outlet lines communicating with the chambers for supplying comburent to the first chamber(s)

and for supplying either fuel to the second chamber(s) and electrolyte to the third chamber(s) or fuel-electrolyte mixture to the second chamber(s); and, for at least one of the first and second chambers, respective closure valves provided in a said inlet line and a said outlet line communicating with said chamber and a reservoir communicating with the inlet or outlet line of said chamber, at a point if said line intermediate the closure valve provided in said line and the fuel cell block, in such a manner that, when the fuel cell is in use, the volume of the reservoir is entirely filled with comburent, fuel or fuel/electrolyte mixture, the pressure compensation reservoir being sealed from contact with the atmosphere and having a fluid-tight movable wall or walls allowing the volume of the reservoir to change in response to changes in the volume of fluid contained therein.

Suitably, when the fuel cell is used for generating electricity with intermittent shutdown by closure of said closure valves for a period between two periods of operation, the pressure compensation reservoir can have a maximum volume at least equal to the volume of fluid consumed in the fuel cell block during the period of closure of said closure valves. Suitably, the reservoir has a flexible wall or wall portion allowing the volume of the reservoir to change in response to changes in the volume of fluid contained therein.

In a fuel cell which is suitable for a method of use wherein said chamber or chambers are supplied with a fluid which comprises an electrochemically active constituent in a proportion C% by volume and an electrochemically inert constituent in a proportion (100-C)% by volume, the pressure compensation reservoir suitably has a maximum volume of at least $(V_c \times C / (100 - C))$ where V_c is the volume of said chamber or chambers of said cell block.

In liquid fuel cells embodying the invention, the pressure compensation reservoir preferably communicates with the inlet or outlet line of a chamber for containing liquid fuel and is disposed at a level higher than the cell block when the cell is oriented for use.

A protective housing can be disposed around the sealed variable-volume reservoir. The outside of the reservoir can be in contact with the atmosphere, or alternatively the housing can seal the pressure compensation reservoir from contact with the atmosphere and means for exerting a pressure higher than atmospheric pressure on said compensation reservoir can be disposed within said housing. Either a gas or a spring can for example be used to exert the pressure.

The invention is described in detail in the following description given by way of

example only of particular, preferred embodiments thereof, illustrated by the accompanying drawings, wherein:-

Figure 1 is a diagram showing an embodiment of a fuel cell according to the invention; and

Figures 2 to 5 diagrammatically illustrate different embodiments of the pressure compensation reservoir of the embodiment of Figure 1.

Referring to Figure 1, a fuel cell comprises a block 1 wherein electrodes delimit a plurality of chambers (not shown). In some types of fuel cell the electrodes delimit chambers fed with a mixture of fuel and electrolyte and chambers receiving a comburent.

However, in the embodiment of Figure 1, the electrodes delimit three kinds of separate chambers, comprising electrolyte chambers fed exclusively with electrolyte, fuel chambers fed with fuel and comburent chambers fed with comburent. In alternative embodiments of the invention the arrangement may be as described above, i.e. some chambers may receive mixtures.

The fuel cell block 1 is provided with inlet ports 2, 3 and 4 and outlet ports 5, 6 and 7 connected to pipes of different circuit feeding the fuel cell respectively with electrolyte, fuel and comburent.

Ports 2 and 5 are respectively connected to pipes 8 and 9 diagrammatically shown by dotted lines and forming part of a circuit feeding the fuel cell with electrolyte, for example, potassium hydroxide, KOH. Ports 3 and 6 are respectively connected to pipes 10 and 11, diagrammatically illustrated by dashed lines and forming part of a fuel feeding circuit of the cell block.

The circuits feeding the fuel cell block 1 respectively with electrolyte and fuel are not shown in the drawing, but it is understood that each of them comprises all the means which are conventionally used to provide for a correct feeding of the fuel cell, for example, a circulation pump, a device for regulating the temperature of the fluid feeding the fuel cell block and so on. All these devices are well known to those skilled in the art and therefore need not be further described in detail.

Ports 4 and 7 of the fuel cell block communicate with the comburent feeding circuit. In the embodiment of the invention illustrated by Figure 1 port 7 is directly connected to pipe 12 of the comburent feeding circuit shown in solid line of the drawing. Port 4 is connected to pipe 13 of the comburent feeding circuit, through a device designated as a whole by reference numeral 14.

Device 14 comprises a pressure compensation reservoir 19 having a maximum volume V_m , delimited by a wall having at least

one deformable portion 20 which transmits the pressure applied on its external surface to the fluid contained therein. The reservoir communicates with the inlet port 4 and with pipe 13 through a pipe 21.

The circuit feeding the fuel cell with comburent comprises closure valves 15 and 16 for the comburent inlet and outlet ports of the fuel cell block, and also comprises a pump 17 providing for the circulation of the comburent in the direction indicated by the arrows, and means diagrammatically shown at 18, for conditioning the comburent, which in this example is a decarbonator, the comburent being air.

However, in other embodiments, for example those employing other comburents, condition 18 may carry out other treatments.

The operation of the fuel cell is as follows. When the fuel cell is connected to an electrical load circuit (not shown), the fuel cell block is simultaneously fed with electrolyte, comburent and fuel by the feeding circuits. The valves 15 and 16 are open and fuel fills reservoir 19, whose volume is then maximum, shown as a solid line in Figure 1. The comburent in reservoir 19 is substantially at the same pressure as the comburent in the fuel cell block.

When the fuel cell is off duty, valves 15 and 16 are closed. The fuel cell block is thus no longer fed with comburent by the feeding circuit, by the fuel supply is continued.

Owing to the phenomenon of electrochemical short-circuit, fuel and comburent consumption occurs, resulting in a decrease of the comburent pressure in the comburent chambers. This pressure decrease is transmitted to the inside of reservoir 19 which permanently communicates with port 4. As a result of the pressure applied to the external surface of the wall 20, reservoir 19 is deformed, thereby diminishing in volume (position shown as dashed line in Figure 1). Consequently the comburent pressure within the reservoir 19 and thus within the fuel cell block is maintained at a substantially constant value for which there is no risk of deformation of the electrodes. The pressure applied to the external surface of reservoir 19 is substantially equal to the comburent pressure in block 1 during the periods of operation of the fuel cell.

Reservoir 19 is so chosen that its maximum volume V_m is at least equal to the volume of the comburent consumed when the fuel cell is off duty.

In the illustrated embodiment device 14 is connected to the inlet port 4, but it would be possible, without departing from the scope of the present invention, to connect device 14 to the outlet port.

When the fuel chambers are separate from the electrolyte chambers, as in the Fig-

ure 1 embodiment, another device similar to device 14 can be connected to the fuel inlet port 2 or the corresponding outlet port, the fuel feeding circuit being then provided with valves similar to valves 15 and 16.

In the case of fuel cells using air as comburent, reservoir 19 should have a maximum volume of at least 25% of the volume formed by the chambers of the block which are fed with air. The volume of any pipe work in communication therewith is of course included in making the calculation of the comburent chamber volume.

Whenever the fuel cell is off duty and all the oxygen of air has been consumed because of the electrochemical short circuit, the comburent chambers are automatically filled with the residual nitrogen, which is an inert gas producing no electrochemical reaction in the fuel cell.

The consumption of fuel and comburent then becomes equal to zero and the fuel cell can be maintained in this state indefinitely without requiring any interruption of the fuel supply.

More generally, when there is introduced into the fuel cell block a mixture of fluids comprising a fluid which does not produce any electrochemical reaction and a fluid which is a reactant in such an electrochemical reaction, the tank 19 will have a maximum volume V_m at least equal to $V_m = V_c \times \frac{C}{1-C}$, wherein V_c is the overall volume of the chambers receiving this mixture of fluids and C a coefficient equal to the proportion by volume of this reactant in the mixture introduced into the fuel cell.

When the comburent is air, V_m is suitably at least 25% of V_c .

Figure 2 shows a diagrammatic cross section of one alternative version of the device 14 of Figure 1, which can be used for reactants feeding the fuel cell block under near-atmospheric pressure.

Reservoir 19 comprises a fluid-tight, flexible membrane 20, made for example of a thin layer of a material having a high flexibility, for example synthetic or natural rubber, or resilient plastics materials. Reservoir 19 communicates via pipe 21, on the one hand, with inlet port 4 of the fuel cell block 1 for the comburent and on the other hand, with pipe 13 of the circuit feeding the fuel cell block with comburent.

In other embodiments the device may be in the comburent circuit or not.

Reservoir 19 is placed in a rigid housing 22 for protection of the membrane 20. The housing 22 is provided with openings 23 to allow passage of the ambient air, whose pressure (the atmospheric pressure in this embodiment) is in contact with the external surface of wall 20.

Figure 3 shows an alternative embodiment of the device 14 illustrated by Figure

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2, wherein reservoir 19 is connected to opening 4 through pipe 21b and to pipe 13 through pipe 21a.

5 Figure 4 illustrates an alternative form of the device 14 illustrated in Figure 3, for use with a fuel cell fed with liquid reactant.

10 In the embodiment of Figure 4, reservoir 19 is vertical and comprises a flexible membrane 20, which avoids any pollution of the liquid by ambient air. The reservoir is supported in a housing 22.

15 When liquid reactants are used, reservoir 19 will be placed at a higher level than the fuel cell block when the fuel cell block is oriented for use.

20 The devices 14 shown in Figures 2 to 4 may, with adaptation, be used in high pressure fuel cells. Thus, for example, in the absence of openings 23 of the casing (Figures 2-5) it is possible to introduce therein a gas at a pressure close to the pressure prevailing within the fuel cell when under operation. It is also possible to use an elastic membrane 20, delimiting such a volume, arranged so that at the minimum volume of reservoir 19, when the fuel cell is off duty membrane 20 is stretched and maintains the fluid in the reservoir 19 at a pressure at least equal to some desired value.

30 Figure 5 shows another device 14 in which the pressure in reservoir 19 results from the application of a force to the external surface of wall 20 through a spring 24.

WHAT WE CLAIM IS:-

35 1. A fuel cell comprising a cell block having therein electrodes delimiting at least one first chamber for containing a comburent, and either at least one second chamber for containing a fuel and at least one third chamber for containing an electrolyte or at least one second chamber for containing a fuel-electrolyte mixture; inlet and outlet lines communicating with the chambers for supplying comburent to the first chamber(s) and for supplying either fuel to the second chamber(s) and electrolyte to the third chamber(s) or fuel-electrolyte mixture to second chamber(s); and, for at least one of the first and second chambers, respective closure valves provided in a said inlet line and a said outlet line communicating with said chamber and a pressure compensation reservoir communicating with the inlet or outlet line of said chamber, at a point of said line intermediate the closure valve provided in said line and the fuel cell block, in such a manner that, when the fuel cell is in use, the volume of the reservoir is entirely filled with comburent, fuel or fuel/electrolyte mixture, the pressure compensation reservoir being sealed from contact with the atmosphere and having a fluid-tight movable wall or walls allowing the volume of the reservoir to change in response to changes in the volume of fluid contained therein.

2. A fuel cell according to claim 1, which has been used for generating electricity with intermittent shutdown by closure of said closure valves for a period between two periods of operation, wherein said pressure compensation reservoir has a maximum volume at least equal to the volume of fluid consumed in the fuel cell block during the period of closure of said closure valves.

3. A fuel cell according to claim 1, which is suitable for a method of use wherein said chamber or chambers are supplied with a fluid which comprises an electrochemically active constituent in a proportion C% by volume and an electromechanically inert constituent in a proportion (100-C)% by volume, and wherein the compensation reservoir has a maximum volume of at least $(V_c \times C / (100 - C))$ where V_c is the volume of said chamber or chambers of said cell block.

4. A fuel cell according to claim 1, 2 or 3, suitable for use with gaseous fuel or comburent and wherein the pressure compensation reservoir communicates with the inlet or outlet line of a chamber for containing said gaseous fuel or comburent.

5. A fuel cell according to claims 3 and 4, suitable for use with air as comburent, and wherein the maximum volume of the compensation reservoir is at least 25% of V_c .

6. A fuel cell according to claim 1, 2 or 3, being a liquid fuel cell, in which the or each pressure compensation reservoir communicates with the inlet or outlet line of a chamber for containing liquid fuel and is disposed at a level higher than the cell block when the cell is oriented for use.

7. A fuel cell according to any preceding claim, wherein the reservoir has a flexible wall or wall portion allowing the volume of the reservoir to change in response to changes in the volume of fluid contained therein.

8. A fuel cell according to claim 7, wherein at least a portion of the wall or walls of said compensation reservoir is made of a membrane of natural or synthetic rubber or other resilient plastics material.

9. A fuel cell according to claim 4, or any claim dependent thereon, wherein a protective housing surrounds said compensation reservoir.

10. A fuel cell according to claim 4 or any claim dependent thereon, being a fuel cell designed for operation at about atmospheric pressure, wherein the outside of said compensation reservoir is in contact with the atmosphere.

11. A fuel cell according to claim 9, wherein said housing seals said pressure compensation reservoir for contact with the atmosphere, and wherein means for exerting a pressure higher than atmospheric pressure on said compensation reservoir is disposed

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within said housing.

12. A fuel cell according to claim 11, wherein said pressure exerting means comprise a gas.

5 13. A fuel cell according to claim 11, wherein said pressure exerting means comprises a spring.

10 14. A fuel cell according to claim 7 or any claim dependent thereon, wherein the or each said reservoir is delimited by a flexible elastic wall which is maintained

stretched regardless of volume variation of the reservoir.

15 15. A fuel cell substantially as hereinbefore described with reference to Figure 1 or Figure 1 as modified by any one of Figures 2 to 5 of the accompanying drawings.

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FIG.1

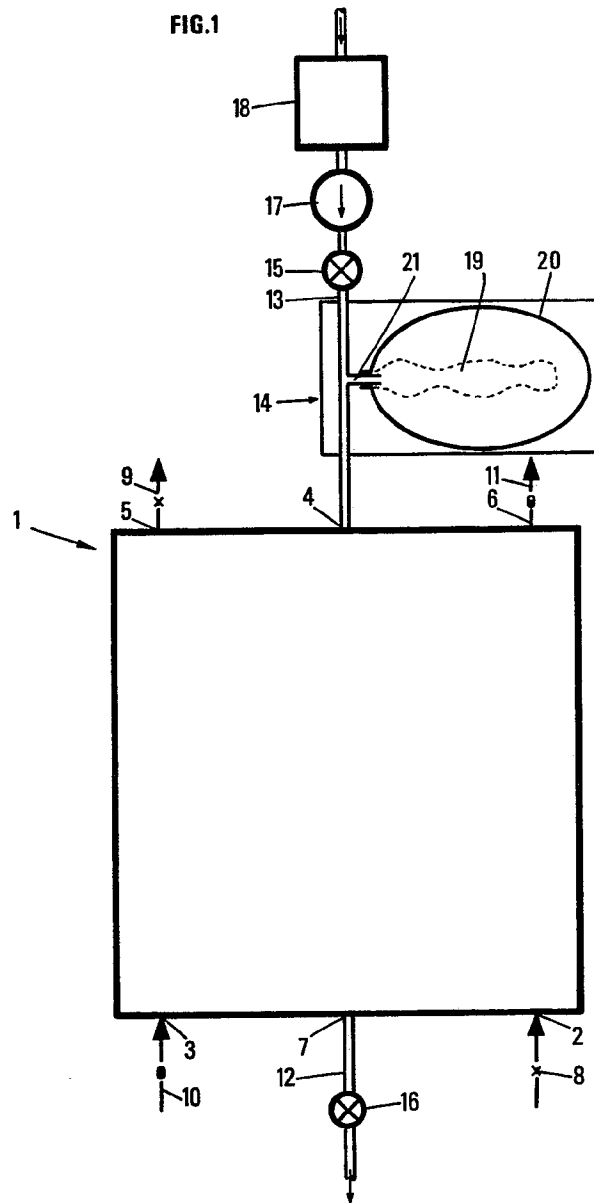


FIG. 2

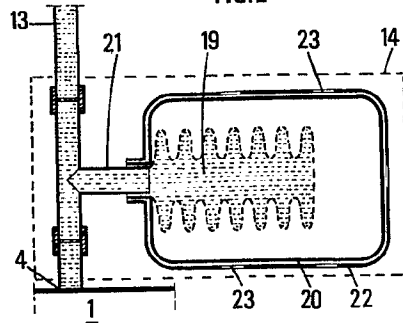


FIG. 3

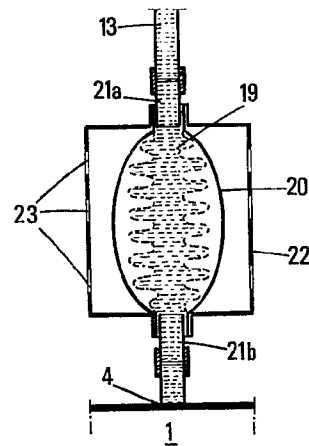


FIG. 4

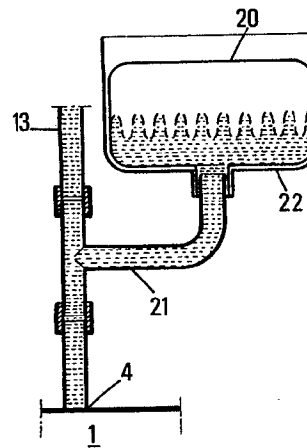


FIG. 5

